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An X-Ray Diffraction Study of a Concentrated Aqueous Sodium Iodide Solution

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Synopsis. X-Ray diffraction measurements of a 7 M NaI aqueous solution showed that iodide ion is surrounded by approximately six water molecules, the I^-–H_2O distance being 3.60 Å and that sodium ion is bonded to about four water molecules at the distance of 2.4 Å.

According to the results so far reported, halide–water distances in the first hydration sphere are about 3.2 Å for Cl^-, 3.4 Å for Br^-, and 3.7 Å for I^-.[1-3] These distances for Cl^- and Br^- ions are in good agreement with the sums of the respective crystal ionic radii and the molecular radius of water. For I^- ion, the anion–water bond length is more than 0.1 Å longer compared with the sum of the crystal radius of iodide ion and the radius of a water molecule. The halide ions are reported to be surrounded by seven to ten water molecules as their closest neighbors.[1-3] However, the number of water molecules around halide ions and the structural arrangement were not definitely determined. The recent X-ray and neutron scattering measurements of LiCl solutions by Narten *et al.*[4] revealed the six-coordinated structure for the hydrated Cl^- ion, although the bond is estimated to be rather weak. Then, questions arise how many water molecules are really coordinated to one iodide ion and if the I^-–H_2O bond is longer by 0.1 Å than the sum of the crystal radius of iodide and the radius of a water molecule.

Lithium and potassium ions were reported to be bonded to four water molecules in the first hydration sphere, their ion-water distances being 2.0 Å[4] and 2.9 Å,[1] respectively. For Na^+ ion, on the contrary, it was suggested that the cation is surrounded by six water molecules, 2.4 Å distant from the central ion.[5] In view of the previous results it seems unlikely that Na^+ ion has a different hydration number from Li^+ and K^+ ions.

In order to reconfirm these points, we have carried out X-ray diffraction measurements of a concentrated sodium iodide solution.

Experimental and Treatment of Data

The NaI aqueous solution was prepared by dissolving recrystallized sodium iodide in water. The concentration of NaI in the solution was found to be 7.009 M from the gravimetric analysis of I^- as AgI.

X-Ray scattering data were obtained at 25 °C on a θ–θ diffractometer (JEOL Co., Tokyo) equipped with a Philips Mo X-ray tube; the details of the measurements are described elsewhere.[6] The measured scattering angle range (2θ) was between 2° and 140°. The intensity data were corrected for background and polarization, and then scaled to absolute intensities $I(\theta)$ according to the ordinary procedures.[6-8] Reduced intensities $i(\theta)$ were extracted by subtraction of independent coherent and incoherent scatterings from the scaled intensities $I(\theta)$.[6]

The radial distribution function $D(r)$ was calculated by means of the Fourier transform of the reduced intensities $i(\theta)$ on the basis of the following equation.

$$D(r) = 4\pi r^2\rho_0 + 2r\pi^{-1}\int_0^{s_{\max}} s\cdot i(s)\cdot M(s)\cdot \sin(rs)\mathrm{d}s \qquad (1)$$

Here ρ_0 is the average scattering density in electron units and $s=4\pi\sin\theta/\lambda$ ($\lambda=0.7107$ Å). The modification function $M(s)$ used is $(f_I^2(0)/f_I^2(s))\cdot\exp(-0.01s^2)$, where $f_I(s)$ is the coherent scattering factor of iodine atom at "angle" s. $s_{\max}$ is the maximum value of s ($\simeq 16.5$ Å^{-1}) reached in the experiments.

Results and Discussion

Figure 1 draws the radial distribution curve $D(r)$ and the differential curve $(D(r)-4\pi r^2\rho_0)$. These curves show three peaks at around 2.4 Å, 3.6 Å, and 4.8 Å. It is readily deduced from the previous results[2,3,5] that the first peak at 2.4 Å is due to the Na^+–OH_2 bond in the first hydration sphere and the second

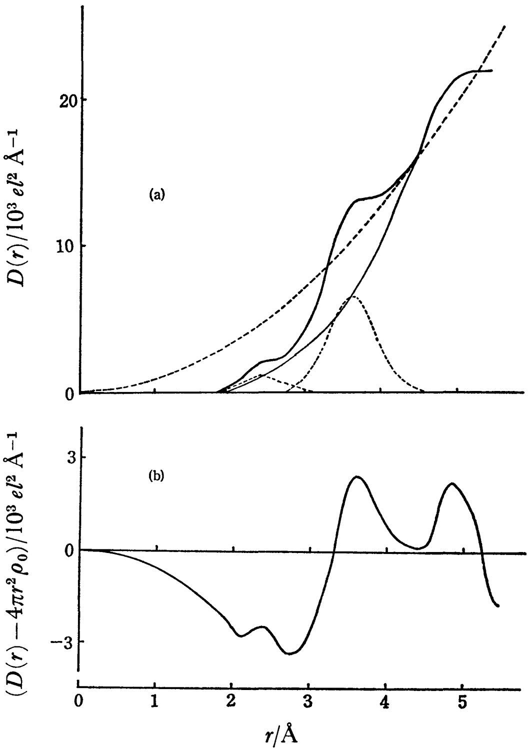

Fig. 1(a). Comparison between the $D(r)$ curve (thick solid line) and the peak shapes calculated for the Na^+-OH_2 and I^--H_2O bonds.
The curve $4\pi r^2\rho_0$ is shown by the thick solid line, the calculated peak shapes by the fine dashed line, and the residual curve by the fine solid line.
(b) Differential curve, $D(r)-4\pi r^2\rho_0$.

peak at 3.6 Å represents the I^-–H_2O bond within the hydrated iodide ion.

The distances for sodium- and iodide–water bonds, and the hydration numbers were evaluated by the trial and error method in such a way that the residual curve brought about by subtraction of the theoretical peaks for the ion–water bonds from the $D(r)$ curve led to a smooth background curve.[6–8] The theoretical peak shapes were produced by the Fourier transform (Eq. (1)) of the theoretical intensities for a given structure calculated by Eq. (2).

$$i_{\text{calc}}(s) = \sum_i \sum_j n_{ij} f_i(s) f_j(s) \frac{\sin(r_{ij}s)}{r_{ij}s} \exp(-b_{ij}s^2) \qquad (2)$$

where $f_i(s)$ and $f_j(s)$ denote the scattering factors of atoms i and j, respectively, and n_{ij}, r_{ij}, and b_{ij} represent the frequency factor, the distance and the temperature factor of the interaction between any atoms i and j, respectively.

In Fig. 1a are illustrated the theoretical peak shapes (fine dashed line) for the Na^+–OH_2 and I^-–H_2O bonds and the resultant residual curve (fine solid line), together with the $D(r)$ curve. The values $r=2.40\pm0.03$ Å, $b=0.004\pm0.002$ Å^2, and n (hydration number)$=4\pm1.5$ for the hydrated Na^+ ion, and $r=3.60\pm0.02$ Å, $b=0.025\pm0.005$ Å^2, and $n=6\pm1$ for the hydrated I^- ion brought about a smooth remainder curve (fine solid line) with no indication of other residual peaks (Fig. 1a). These values were refined by direct comparison of the reduced intensities $s\cdot i(s)$ and the theoretical ones calculated from Eq. (2). The satisfactory agreement was obtained between the observed and calculated intensities in the s region larger than 3.5 Å^{-1}.

In conclusion, the distance (2.4 Å) for the Na^+–OH_2 bond is in good agreement with that reported previously.[5] On the contrary, the I^-–H_2O distance of 3.60 Å found in this work is shorter than that reported by Lawrence and Kruh in concentrated alkali iodide solutions.[2] Our I^-–H_2O bond length corresponds to the sum of the crystalline radius of I^- ion (2.16 Å)[9] and the radius of a water molecule (1.4 Å), as is true for the distances of the Cl^-–H_2O and Br^-–H_2O bonds.[2–4] The hydration number of I^- ion found in this work was a little smaller than that reported previously,[2,3] but the same as that of Cl^- ion.[4] Although the number of water molecules coordinated to Na^+ ion was not definitely determined because of the small scattering power of Na, our result showed that $n=4$ is more probable than 6.

It was difficult to clearly identify the asymmetric peak ranging from 4.5 Å to 5.2 Å; the peak may be ascribed to the Na^+–OH_2 and I^-–H_2O interactions in their second hydration spheres and H_2O–H_2O interactions within the hydrated I^- ion.

References

1) G. W. Brady and J. T. Krause, *J. Chem. Phys.*, **27**, 304 (1957).

2) R. M. Lawrence and R. F. Kruh, *ibid.*, **47**, 4758 (1967).

3) G. Licheri, G. Piccaluga, and G. Pinna, *J. Appl. Cryst.*, **6**, 392 (1973).

4) A. H. Narten, F. Vaslow, and H. A. Levy, *J. Chem. Phys.*, **58**, 5017 (1973).

5) O. Devik, C. Finbak, and O. Rönning, *Tidsskr. Kjemi. Bergvesen Met.*, **4**, 50 (1944).

6) H. Ohtaki, M. Maeda, and S. Ito, This Bulletin, **47**, 2217 (1974).

7) H. Ohtaki and M. Maeda, *ibid.*, **47**, 2197 (1974).

8) M. Maeda, H. Ohtaki, and G. Johansson, *ibid.*, **47**, 2229 (1974).

9) L. Pauling, "General Chemistry," 2nd Ed., Freeman, San Francisco and London (1953), p. 217.